PREPARATION AND ANALYTICAL APPLICATION OF POLYELECTROLYTE GELS

DISSERTATION

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Dedicated
to
my Parents

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Certified that the work embodied in this dissertation entitled " Preparation and application of Polyelectrolytes gels" is the result of the original research work carried out by MS. GHAZIA ASIF under my supervision and is suitable for submission for the Master of Philosophy in Chemistry.

(Saidul Zafar Qureshi)

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Ghazia Asif

GHAZIA ASIF

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CHAPTER I

INTRODUCTION

Analytical Chemistry deals the problem of qualitative and quantitative analysis using classical and modern methods of instrumental techniques. Many important factors are considered in choosing the analytical methods, say concentration range, accuracy, sensitivity, selectivity, time and cost of analysis.

A separation procedure can be used for purification, qualitative identification or quantitative determination which are systematically summarized in Table I.

Chromatography, which is one of the most versatile techniques, has the unique position of being applicable to all types of problems and has undergone explosive growth in the last 25 years. Chromatography can be classified into different types depending on their stationary and mobile phases. Ion exchange chromatography in which beads of ion exchanger are used as sorbent, has become an important tool in resolving a complex mixture, which is rather difficult by other means. This is helpful in the separation of ions having similar chemical and physical properties. The theoretical principle involved in the separation process is the differences in the preferential uptake of ionic species by ion exchange. It has also proved its excellence in the field of biological, organic and inorganic chemistry.

TABLES- I

METHODS OF SEPARATION

Method	Principle
Precipitation	Difference in solubility
Distillation	Difference in volatility
Sublimation	Difference in vapour pressure
Extraction	Difference in solubility in two phases
Crystallization	Property of solubility usually at lower temp.
Zone refining	Crystallization usually at elevated temp.
	CHROMATOGRAPHIC METHODS
Adsorption Column Chromatography	Distribution of solute between a solid and liquid phase in a column
Partition column chrom.	Distribution of a solute between two liquids on a column.
Ion exchange chrom.	Exchange of ions

Ion exchange phenomenon was first observed and described by Thompson an English agriculturist(1). He found that ammonium sulphate was converted to calcium sulfate. But he communicated his findings to Way (2), a consulting chemist of the Royal agricultural society who explained ion exchange phenomenon in soil as given below

$$Ca(Soil) + (NH_4)_2\ SO_4 \rightleftharpoons 2NH_4\ Soil + CaSO_4$$

Harm(3) in 1896 successfully removed sodium and potassium ions from sugar beat. Juice by naturally occuring cation exchange silicate material. Gans (4) successfully applied by self synthesizing inorganic exchange material of alumino silicate ($Na_2Al_2Si_3O_{10}$) to water softening and sugar treatment. Then Adams and Holms (5) observed that the crushed phonograph records exhibit ion exchange properties. This led remarkable evolution to the synthesis of organic ion exchange resins.

The commercial production and improvement of synthetic resin by Holms and Farbenindustrie soon followed. The really modern era in ion-exchange technology began in 1944 when D'Alelio of the German Electric Company's Pittsfield laboratories synthesized resins from polystyrene (6). Polystyrene resins which compared to the earlier resins, possessed greatly improved capacity and chemical and mechanical stability. Emulsion polymerization of swollen styrene and divinyl benzene

followed by sulfonation yields strong polystyrene poly-sulfonates resin with " adjustable" cross-linking. Copoly-merization of methaoxylic acid with divinyl benzene resulted in a weak cation exchange resin of lesser acid strength and high capacity.

Further extensive research and studies on inorganic ion exchange sorbents have been carried out during the last three decades owing to their admirable contribution in the field of nuclear energy, hydrometallurgy of rare earth elements, pre-paration of high purity materials, water purification etc. This is inspiring many new scientist to synthesize new highly selective ion exchange materials mechanically stable resistant to chemicals, temperature changes and radiation and of more widely applicable properties as compared to other ion exchange materials e.g. aluminosilicates.

The work upto 1963 has been summed up by Amphlett (7) in his monograph " Inorganic Ion exchangers" in a concise and excellent way. Further developments have been carried out by following scientists in the field of inorganic ion exchangers; Peparak, Vesley (8), Clearfield (9,10), Alberti (11,12), Walton (13-16), Volkhim (17), Gill (18).

The classification of inorganic ion exchange materials on the basis of the chemical characteristics of ion exchanging

species, as proposed by Versely (8) is as follows:

1. Hydrous oxides
2. Acidic Salts of multivalent metals
3. Salts of heteropoly acids
4. Insoluble ferrocyanides
5. Alumino Silicates
6. Certain other substances (e.g. Synthetic apatites sulfides, alkaline earth sulfates.)

A large number of scientific papers projecting structural properties of ion exchanger and their analytical applications have been published. A wide range of observations on ion-exchange sorption by hydrous oxides can be interpreted on the basis of reversible ion-exchange equilibria. Hydrous oxides are divided into two main types; particle hydrates, those like ZrO_2 and SnO_2 for which ion-exchange occurs only on the surface and framework hydrates which contain cavities or tunnels in which exchangeable ions reside such as the hydrous oxides of antimony and manganese (19). Figure .1 shows the various forms of MnO_2 with tunnel structures.

The most studied group is the quadrivalent metal oxides which may behave either as cation or anion exchangers, depending upon the basicity of the central atom and the strength of the metal oxygen bond relative to that of the oxygen-hydrogen bond in the hydroxyl group. It is still not clear which of

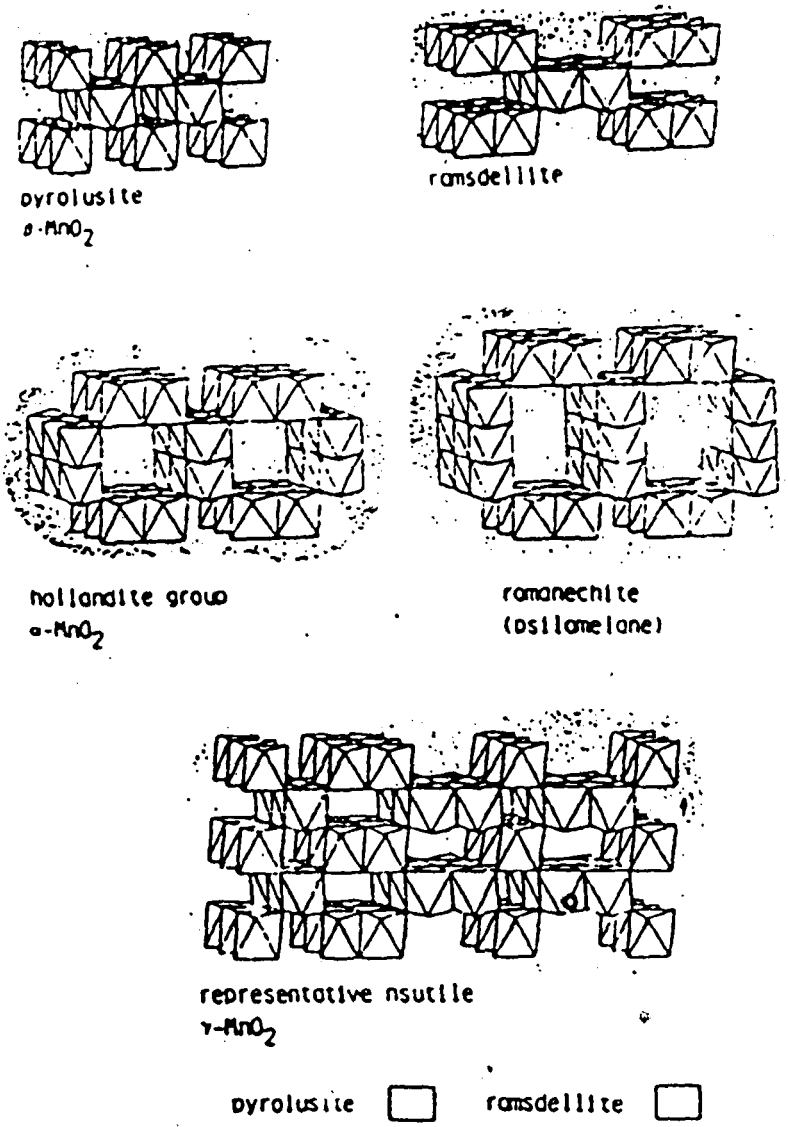


Figure 1 Various forms of MnO_2 with tunnel structures. (From Burns, R. G.; Burns, M. B. *Manganese Dioxide Symposium* Tokyo, 1981; Vol 2, Chapter 6).

the following mechanism best represents the situation

$$M - OH \rightleftharpoons M^+ + OH^- \quad \ldots (a)$$

$$M - OH \rightleftharpoons M\text{-}O^- + H^+ \quad \ldots (b)$$

(M represents central atom)

Scheme (a) is favoured by acid conditions, when the substance can function as an anion-exchanger, the scheme (b) by alkaline conditions when the substance can function as a cation-exchanger. Near the isoelectric point of the oxide (25) dissociation according to both schemes can take place and both types of exchange may occur simultaneously.

The acidic salts of quadrivalent metals have been the most intensively studied group of synthetic inorganic ion exchangers. This group of compounds consists of phosphates, arsenates and mixed arsenates-phosphates of both IVA, IVB and V groups. A number of comprehensive reviews on various aspects of the properties and behavior of these compounds have been published recently (55,56) including materials aspects (57), ion exchange (58), catalysis (59) and membranes (60). They are usually layered structure of α type e.g. α-titanium arsenate, α-titanium phosphate α-Zirconium phosphate. The earlier studies on zirconium phosphates are mostly concerned with amorphous materials (7,25,26,27).

The preparation of gelatinous amorphous gel is carried out by mixing zirconium salt solution with phosphoric acid at

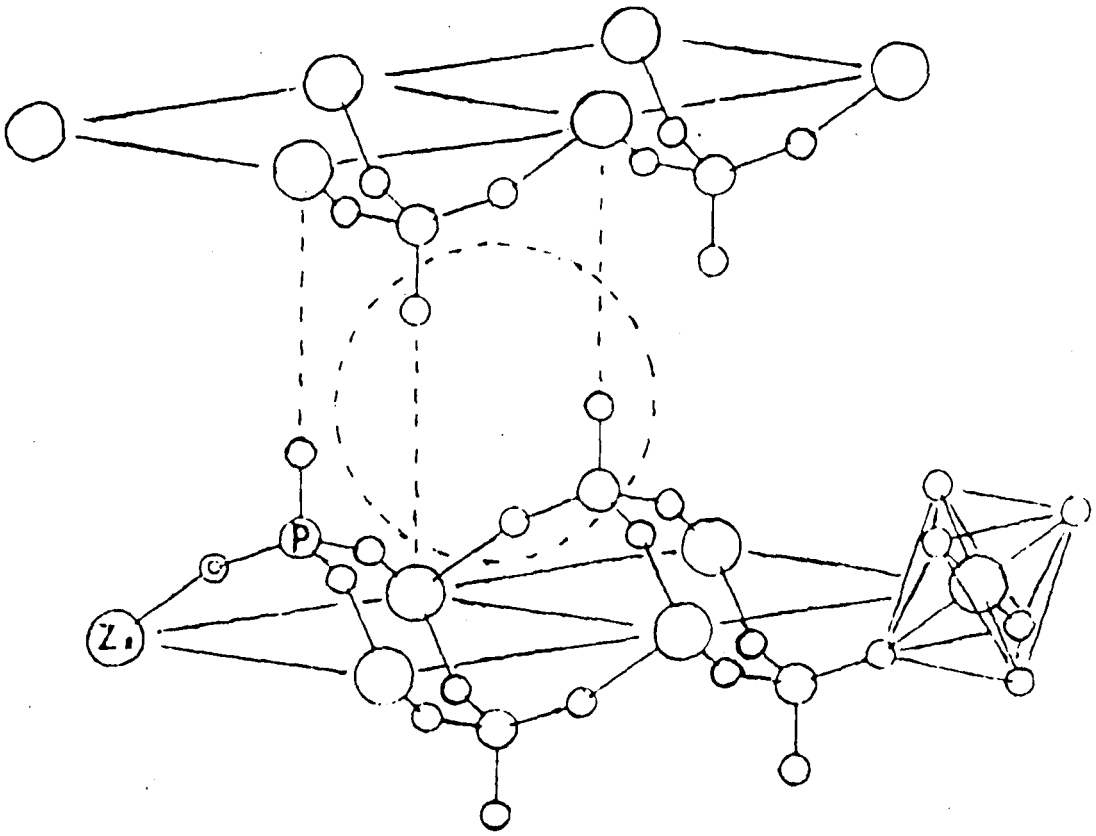


Fig 2 Schematic illustration of the structure of α-zirconium phosphate.

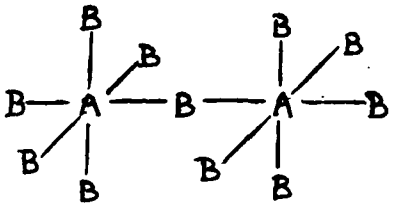
room temperature. According to the preparation condition materials with P/Zr ratios of .5-2.1 are formed(9,28-34). While the thermal treatment of amorphous materials with phosphoric acid(35-37) or refluxing them with > 2.5M phosphoric acid (7,9,36-39) leads to the formation of semi-crystalline and crystalline forms respectively. Zirconium bis monohydrophosphate (α-ZrP), was prepared by refluxing the amorphous gel in 10 to 15M phosphoric acid. The structure is layered and the compound is monoclinic with unit cell dimensions of a=9.076, b=5.298, c=16.22A° and β=111.5° with formula $Zr(HPO_4)_2.2H_2O$ (20-24). A simplified schematic diagram illustrating the essential features of α-ZP, proposed by clearfield and stynes (20), is given in Fig.(2). Each layer can be regarded as a two-dimensionally infinite complex molecule, which consists of a sheet of roughly coplanar zirconium atoms sandwiched between the two sheets of monohydrogen phosphate groups. Each zirconium atom is coordinated by six oxygen atoms arranged octahedrally about the zirconium atom.

The sequence in which the layers are packed together is such that neighboring monohydrogen phosphate groups from adjacent layers are staggered and do not lie directly opposite one another. This packing sequence creates zeolytic cavities in the inter-layer region. One of these cavities is indicated by the dashed circle in Fig.2. There is one such cavity per

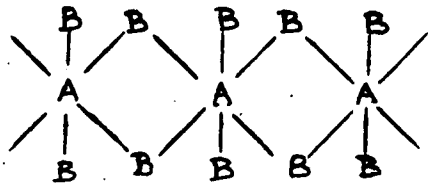
formula unit, $Zr(HPO_4)_2H_2O$ and water molecule lie in this cavity. The interlayer separation in the αZP structure is 7.6°A. The two layers of αZrP are schematically represented in fig.4a.

The concept of layer, chain and coordination lattice structures in octahedra and tetrahedra can be understood from the following repeat units:

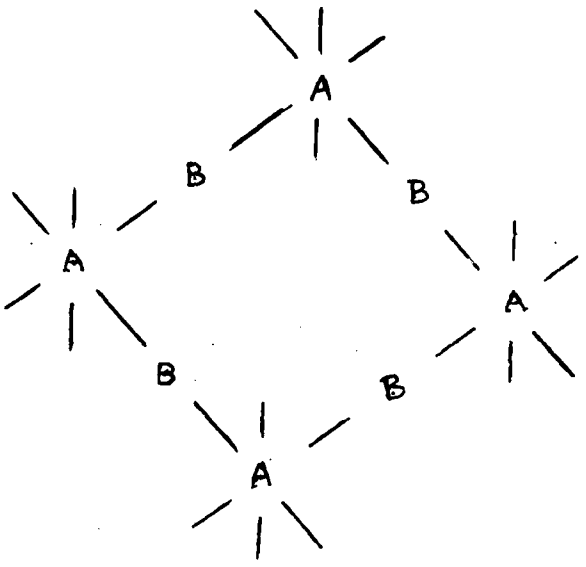
I AB_6 octahedra unit cells



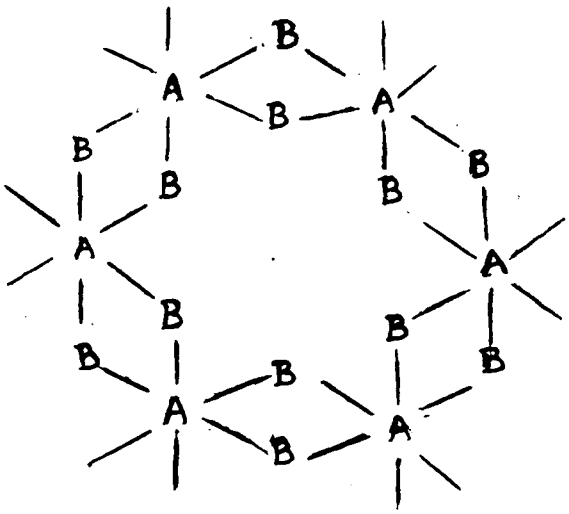
Endless chain with AB_5



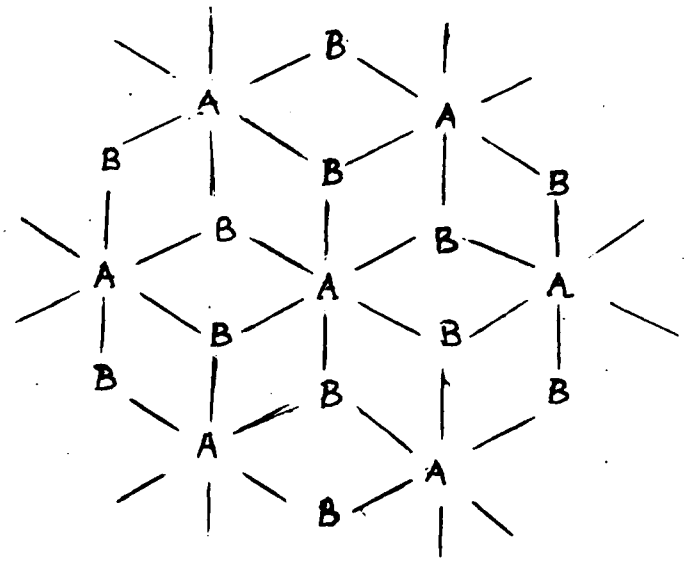
Endless chain with AB_4 joined at two apexes



layered two dimensional with AB_4 stoichiometry

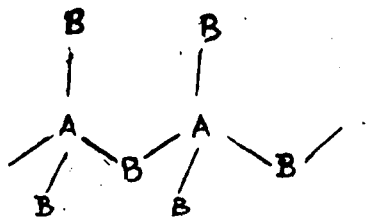


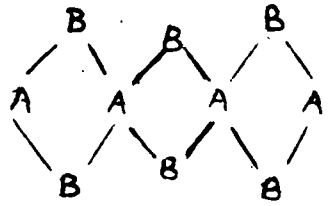
Joined by edges. Layered with AB_3 stoichiometry



Joined to six neighbours by their edges with AB_2 stoichiometry

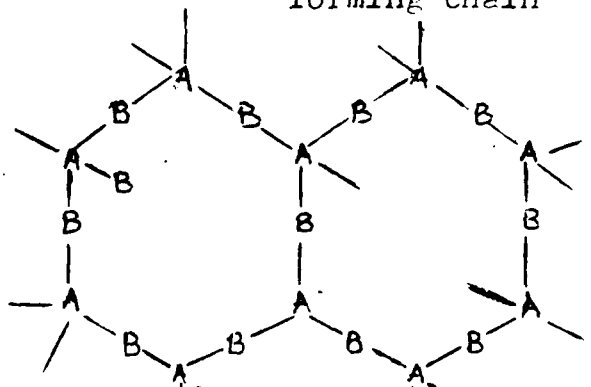
II AB_4 tetrahedral Unit Cells





Jointed to two neighbouring cells at their apexes forming chain structure

AB_2 composition forming chain



layered structure of A_2O_5 stoichiometry

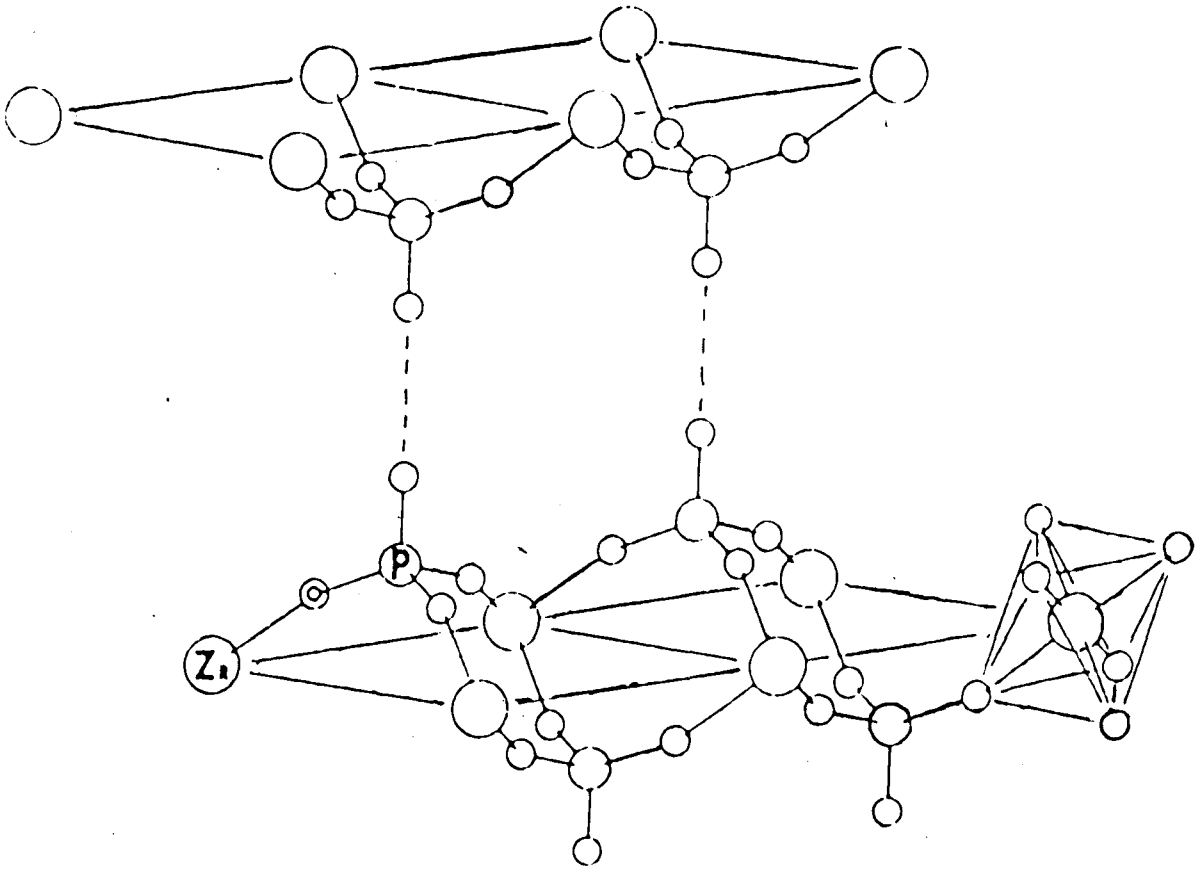


Fig. 3 Schematic illustration of the model structure proposed for β- and γ-zirconium phosphate.

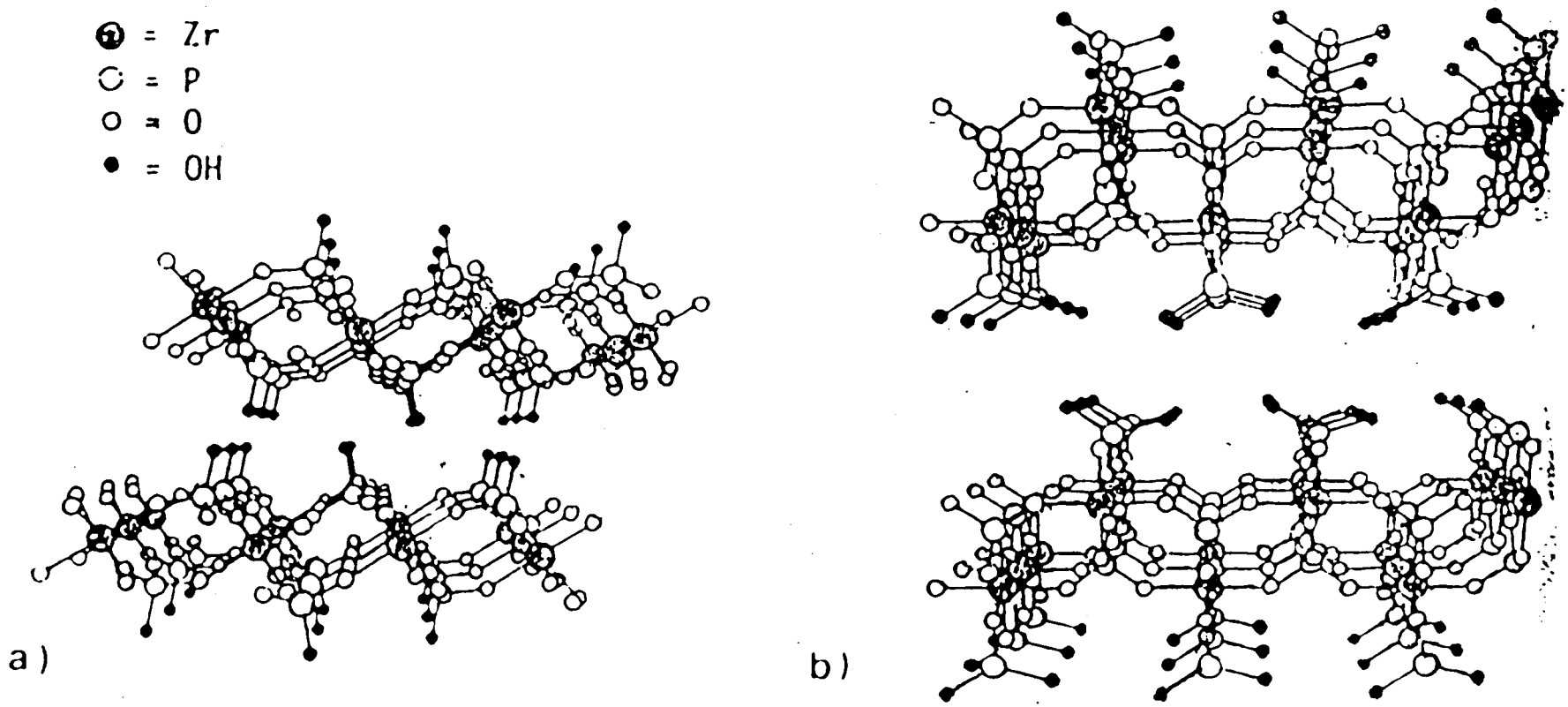


Fig. 4 Representation of two layers of α-$Zr(HOPO_3)_2$ (a) and γ $Zr(PO_4)(H_2PO_4)$ (b) as viewed down the b-axis.

Clearfield proposed that the structures of β.ZrP and -ZrP are also layered as represented in Fig. 3.

Acidic salts with layered structures of β and types contain larger interlayer spacing than α Zr P, but the atoms in their layers lie directly over one another Fig. 4b. The β and phases corresponding to $Zr(HPO_4)_2$ and $Zr(HPO_4)_2 2H_2O$ respectively, are prepared by refluxing the solutions of $ZrOCl_2$ with NaH_2PO_4 in 3M hydrochloric acid. Drying over anhydrous $CaSO_4$ leads to the formation of β-zirconium phosphate, air dried product corresponds to -zirconium phosphate (40). These sorbents can adsorb cations with larger dimensions, such as Cs^+.

A few important applications of zirconium phosphate exchangers are as follows:

1. Purification of reactors coolants (61)
2. Decontamination of D_2O (62)
3. Decontamination of radioactive waste water (63)
4. Cs^{137} from a reprocessing solution (64)
5. Pu^{4+}, separation from irradiated uranium (65)

A number of three component ion exchangers have also been prepared in which parent acid belong to the class of 12-heteropoly acids having the general formula $H_3XY_{12}O_{40}xnH_2O$ where x may be phosphorous, arsenic, silicon, germanium and

boron and Y different element such as molybdenum, tungsten and Vanadium. Much of subsequent investigation of the ion exchange properties of these salts have been carried out by Smith & Robb (66). Three component ion exchangers show superiority over simple salts mainly in three aspects. They are more thermally and chemically stable, more selective (67). Synthesis and properties of two component and three component ion exchangers have been summarized in table 2 and 3 respectively.

In the recent years pillaring of layered structures have been achieved by intercalation. Phosphate and phosphonate metals constitute a large family of compounds with a variety of structures (fibrous, layered, skeleton) and different functionalities. The ion exchange and intercalation behaviour mainly of α-ZrP was reported by Constantino and Vivani (42).

Recent progress in the intercalation chemistry of α-ZrP has led to the preparation of numerous new intercalation products. Those with aliazoles and diazines (43) and with aminoalcohols were found to have a proton conductivity higher than $\alpha\text{-}Zr(HPO_4)_2$. The intercalation compound with tetra methyl benzene contain 0.35 mol of guest per mol of Zr, arranged as a mono layer of molecules tilted at an angle of 60° with respect to the layer plane as explained earlier.

TABLE II

Properties of some two component ion exchangers

S.No.	Material	Type of Exchanger	Composition	Emperical Formula	1EC	Selectivity	References
1.	Zirconium phosphate	Amorphous	P/Zr=.5-2.5	$Zr(OH)PO_4$	-	Cs^+ Rb^+ K^+ Na^+	25,36,37,67, 68
				$ZrO(HPO_4)$	-	Eu^{3+}, Sr^{2+}, Co^{2+}	
				$Zr_3(PO_4)_4$	-	Ni^{2+}, Zn^{2+}	
				$Zr(HPO_4)(H_2PO_4)OH$			
				$Zr(HPO_4)_2.H_2O$	-		
		Semicrys-talline	-	-	-	Li^+ K^+ H^+ Cs^+	69, 70
		Crystalline	-	$Zr(HPO_4)_2H_2O$	-	Sr^{2+}, UO_2^{2+}, Ce^{3+}	
2.	Zirconium antimonate	Amorphous	-	$ZrO_2Sb_2O_5.nH_2O$	-	Na^+, K^+, NH_4^+	71
3.	Zirconium arsenate	Amorphous	Ar/Zr 1.53 - 1.96	$ZrO_2.84As_2O_5nH_2O$	4.3	Na^+, K^+, Cs^+	72 - 74
		Crystalline	-	$Zr(HAsO_4)_2.H_2O$	5.10	Li^+, Na^+, K^+	74
4.	Zirconium tellurate	Amorphous	-	$Zr(H\ TeO_6).4H_2O$	2.8	-	75, 76
5.	Zirconium oxalate	Crystalline	-	$Zr(OH)C_2O_4$	2.5	Alkali metal	77

TABLE - III

PROPERTIES OF SOME THREE COMPONENT ION EXCHANGERS

S.No.	Material	Type of exchanger	Composition	Emperical formula	I.E.C. meq/g	Selectivity	Reference
1.	Zirconium molybdophosphate	-	-	-	1.6	-	78
2.	Zirconium molybdovanadate	-	Zr:V:Mo 1.68:1.00:0.088 3.33:1.00:0.28 6.15:1.00:0.82	-	-	Li^+ Na^+	79
3.	Zirconium arsenophosphate	Crystalline	Zr : As : P 1 : 1 : 1	$Zr(HAsO_4)(HPO_4).H_2O$	5.85	-	80
		Amorphous	-	-	-	Rb^+, Ag^+, Ti^+	81,82
4.	Zirconium phospholodate	Amorphous	-	-	-	-	83
5.	Zirconium arsenosilicate	Crystalline	-	-	-	Hg^{2+}	84
6.	Zirconium Iodomolybdate	Amorphous	Zr : I : Mo	$[(ZrO)_3(OH)(IO_3)(HMoO_4)_4]_n$. $6nH_2O$	1.54	Hg^{2+} Th^{4+}	85,86
7.	Zirconium selenophosphate	Amorphous	Zr : Se : P 5.06:2.0:4.05	$[(ZrO)_5(OH)_4(HSeO_3)_2(H_2PO_4)_4]_n.2nH_2O$	1.51	Fe^{3+}, Th^{4+}	87

Two different strategies are currently followed to obtain microporous solids for molecular sieving and shape selective catalysis based on zirconium phosphates and phosphonates.

According to the first one material similar to the pillared clays can be prepared by intercalation of suitable large cation or organic molecules (that act as pillars) between the layers of zirconium phosphate or its derivatives.

In case of clays one may adjust the pore size by varying the size of the pillars and/or the spacing between them.

Another view point was put forwarded that during the preparation of zirconium diphosphonates $ZrR(PO_3)_2$, the R group link adjacent to α-layers and act as pillars (44). It was found that some zirconium diphosphate phosphonates might be obtained as mesoporous solids with high surface area (300-500 m^2/g) and a narrow distribution of mesopores in the range 20-40A° (45). Fig.5 is showing the pillaring by R group in $ZrR(PO_3)_2$. The distance between adjacent R groups is only 5.3 A°. The interlayer distances of functionalized α-zirconium phosphate and diimine intercalates of γ-zirconium phosphate are summarized in Tables 4 & 5.

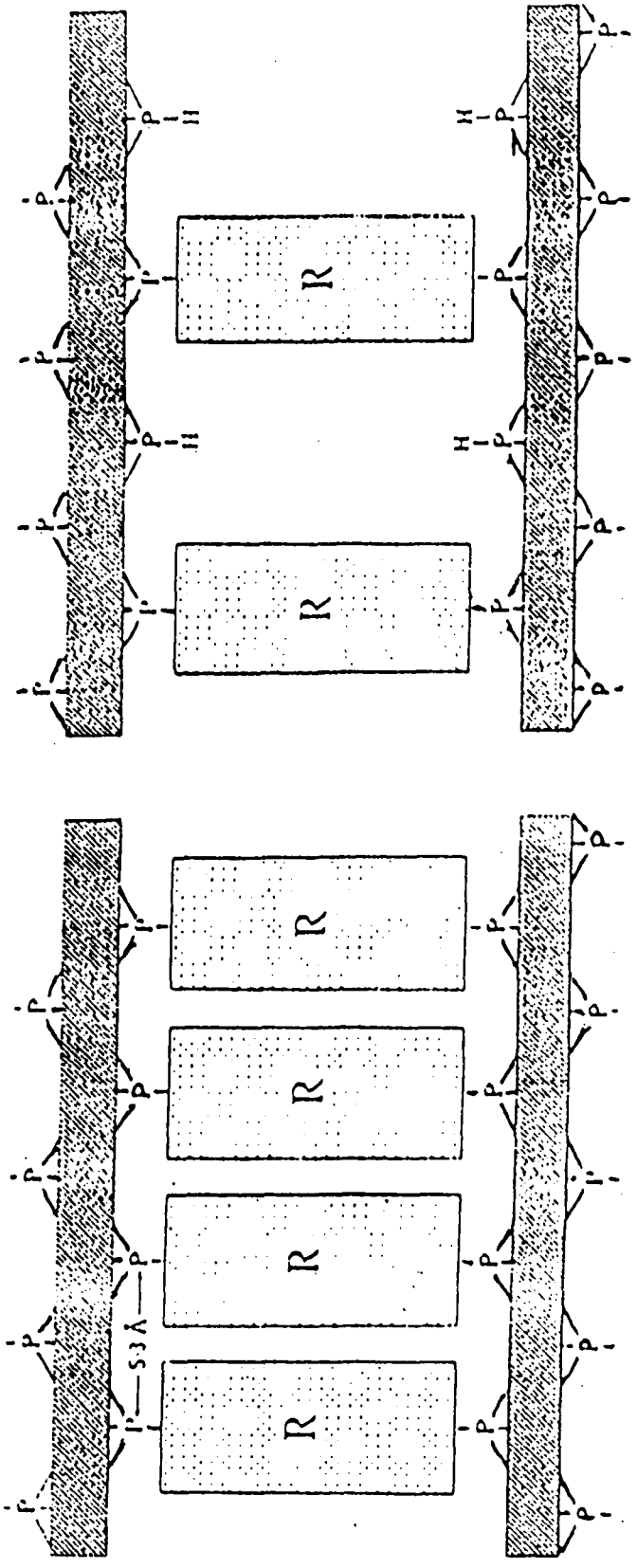

R
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TABLE-4 Formulae and interlayer distance of functionalized zirconium phosphates.

Compound	interlayer distance(A°)
$Zr(HOCH_2PO_3)_2H\ O$	10.1
$Zr(HOOCCH_2PO_3)_2$	11.1
$Zr(HO\ SCH_2)_3PO_3)_2$	18.8
$Zr(NO\ NH_3CH_2CH_2PO_3)_2 2H_2O$	14.6
$Zr(H_2NHOOC\ CHCH_2PO_3)_2$	14.4
$Zr(HOPO_3)_{0.67}\ (HPO_3)_{1.33}\cdot 5H_2O$	12.9
$Zr(HOOCCH_2CH_2PO_3)(HOPO_3).2H_2O$	10.2
$Zr(HOPO_3)_{1.1}\ (C_6H_5PO_3)_9.H_2O$	24.8

TABLE 5 Intercalation of α-Diimine in γ-ZrP

α-Diimine	Reaction temp i	Contact time n	Interlayer distance A°	X	Y
phen	50	48	17.40	.34	1.15
bpy	25	48	13.71	.18	.52
terpy	50	48	14.89	.15	.96

X and Y denote the moles of α-diimine and hydration water in formula unit of -ZrP, Phen - 1.10 phenanthroline, bpy-2,2' bipyridine terpy- terpyridine.

Intercalation of pyridine derivatives such as pyridine and 4-Vinyl pyridine(4VP) into lithium rectorite (clay) have been carried out (46) without a cation exchange process. Formation of hydrogen bond with interlayer water and coordination bond to inter-layer lithium cation are the main processes for these intercalation. The degree of the involvement of both the processes depends upon proton affinities (PAs) of guest compounds.

In an attempt (47) to prepare new type of host materials for molecular recognizing catalysis, synthetic clay compounds were modified by the methods of ion-exchange of simple or complex cations and chemical anchoring of metal complexes. These products were studied in terms of shape selective decomposition of alcohols and molecular recognizing hydrogenation of olefines. Thus new types of catalytic sites were prepared on the layer structures of clays by following methods:

1. Ion exchange with acidic metal cations to form interlayer acid sites.
2. Ion-exchange and reduction of metal complexes to form interlayer fine metal particles.
3. Ion exchange with large metal complexes to form immobilized molecular complex as catalytic sites.
4. Amination of inner surface to form chemically anchored stable metal complexes. Catalyst test were carried out

in gas solid and liquid-solid heterogeneous systems for the decomposition of C_2 - C_4 alcohols and the hydrogenation of various acetylenes and olefines. Chemically anchored Pd in schematically represented in Fig. 6. The effects of interlayer anchoring were more apparent on the catalysis of bulky olefines between narrow clearance spaces.

The two dimensional spaces between the silicate sheets can accomodate neutral molecules such as water, alcohols, amines as well as various metal and complex cations by ion exchange (48).

New catalytic fields designed in the host-guest complex based on modified clay compounds has been demonstrated as on of the new potential materials to develop molecular recognizing catalysis (47).

There is a continuing need to find new ion-exchangers which are capable of treating radio active nuclear effluent(49) and to remove toxic substances from aqueous effluents. Hydrogen phosphates of tetravalent metals have been the subject of considerable study in recent years because of their ion-exchange and intercalation properties (50). It was also observed that α-intercalation of mono amines such as allylamine or n-propyl amine into Tin(IV) hydrogen phosphate, α-$Sn(HPO_4)_2$

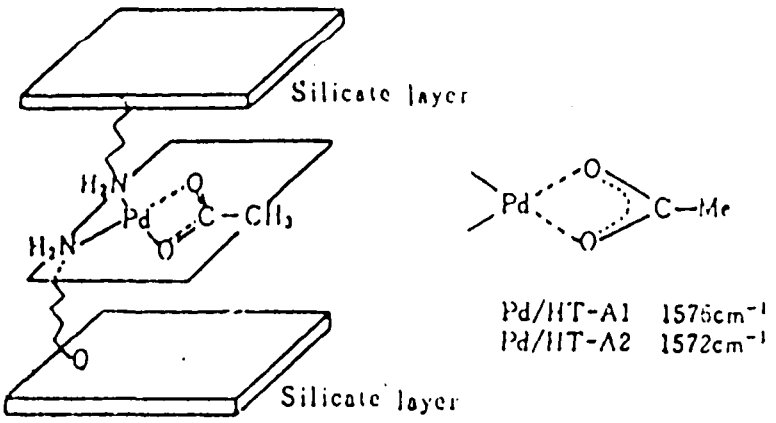

Fig.6 Structure Model of Chemically Anchored Pd-Complex on LHT

H_2O(αSnP) doubles the extraction capacity relative to the parent α-SnP and ion-exchange reactions of the intercalates were rapid (51).

The intercalated α-$Sn(HPO_4)_2H_2O$ have been studied by Hudson and Workman (51). Previous studies on α-SnP have indicated that it is a layered compound which has an interlayer spacing of 0.78 nm but the structures of the NNBD and propylamine intercalates (SnP-NNBD and Sn P-PrA) are represented in Fig.7 and 8 showing interlayer spacing 1.35 nm and 1.67 nm respectively. Thus the interlayer distance can be changed by intercalation. Interlayer distance of α-SnP for different amines to given in table 6.

TABLE 6. Interlayer distance and composition of some αSnP/amine intercalation compounds (51).

Amine	Solvent	Interlayer spacing (nm)	Composition Molamine per Mol αSnP
Allylamine	Water	1.56	2.0
Allylamine	Toluene	1.67	2.0
Propylamine	water	1.75	2.0
Propylamine	Toluene	1.86	2.0
1.2 Diaminoethane	Toluene	1.08	1.2
Triethylamine	Toluene	1.34	.7
Tetraethylene pentamine	Water	1.89	.4

Another new step in the field of inorganic ion exchanger is loading with different substances and making it more selective towards a particular ion/ions such as sequential collection of selenium(IV) and selenium(VI) by the use of an anion exchange resin loaded with bismuthol II sulphonic acid ligand (52).

In another modification of anion exchange resin with thiols sulfonates derivatives of dithiozone and other thiols were immobilized firmly by an anion-exchange resin. And these chelating agents were used in collecting and determining metal ions (53) and titanium diethanolamine was prepared by modification of hydrous titanium oxide (54). This material possessed a metal sorption capacity of .6 to .9 mmoles g^{-1} and showed selective retention of certain metal ions. It has been found useful for analytical sorption of Cd(II) from Pb(II), Cu(II) and Hg(II); Tn(IV) and Hg(II) and Mn(II) from Fe(III). The sorption rates were also determined.

Thus new developments in ion-exchange have many fold enhanced its analytical importance and have attracted many scientist to synthesize new ion exchanger with high speed, sensitivity and selectivity by using intercalates or loading with different substances and using multicomponent exchangers.

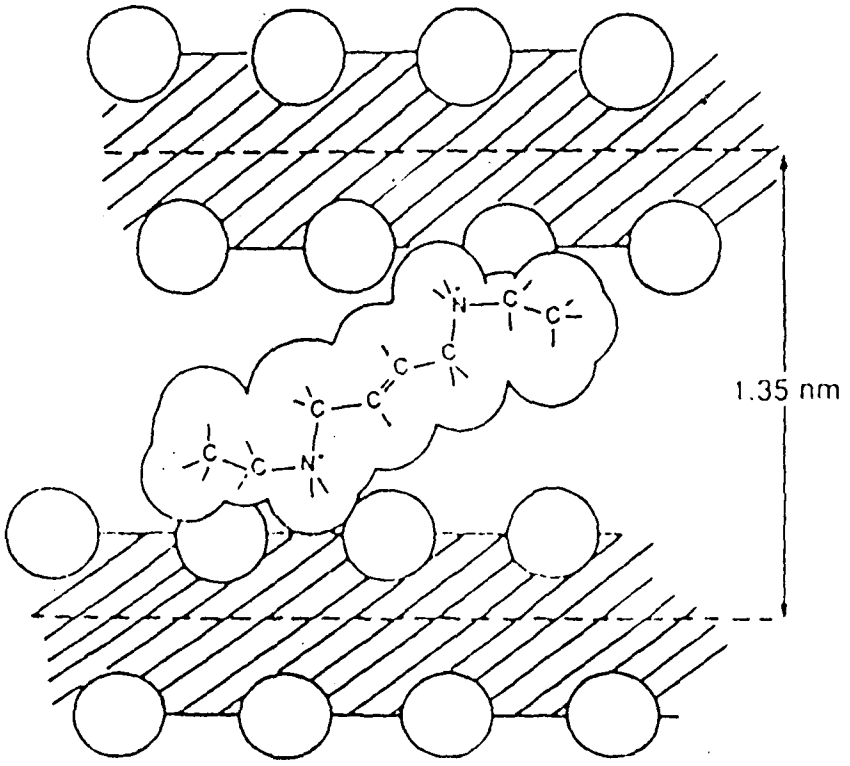

Fig. 7 Idealised structure of the SnP-NNBD intercalation compound

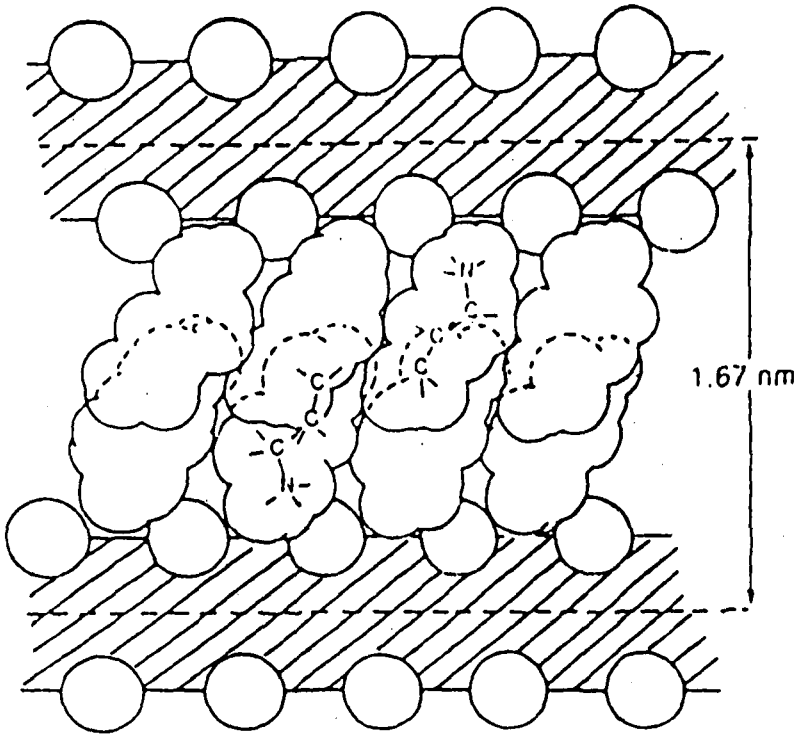

Fig. 8 Idealised structure of the SnP-PrA intercalation compound

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CHAPTER II

PREPARATION AND CHARACTERIZATION OF NEW ZIRCONIUM PIPERIDINE THIOGLYCOLATE EXCHANGER

INTRODUCTION

New developments in inorganic ion exchangers have increased its analytical applications. There is a continuing need to find new ion exchangers which are capable of treating radioactive nuclear effluent (1) and to remove toxic substances from aqueous effluents. Chelating resin are often used for preconcentration of metal ions. A number of chelating resins have been synthesized (2). Chelating resin containing thiol group as a soft base are expected to offer several advantages in the preconcentration of heavy metal ions a soft acid due to their selectivity and larger concentration factors than common iminodiacetic acid type resion (3).

In this work a new idea has been developed to give a dual character to the exchanger. Anion, cation and amphoteric, ion exchangers have been prepared in the past, however to attach an amine group in order to act as anion exchanger exhibiting clearly the anion exchange properties and to intercalate a thioglycolate group between the layers of ZrO_2 to coordinate exclusively some of the transition metal ions. The work is in progress and there is hope of achieving interesting results.

EXPERIMENTAL

Reagent:

Zirconium oxychloride(BDH), piperidine(Loba Chemicals, India), thioglycolic acid(S.D. Fine Chem.Ltd. India)and other Chemicals of analyt. grade were used.

Apparatus:

A Bausch and Lomb spectronic 20 and spectronic 1001 were used for spectrophotometric measurements. Elico Li-10 pH meter was used for pH measurement.

Synthesis:

Various samples of exchanger were prepared by mixing an aqueous solution of 0.2M zirconium oxychloride, piperidine and thioglycolic acid under different sets of condition as listed in Table 7. The gel formed was thoroughly stirred on a magnetic stirrer at 50°C for 4 hrs. The gel so formed was allowed to settle down for 24 hrs, washed several times with distilled water to remove excess reagents and finally filtered under suction. It was then dried at 60°C in an oven. The dried material was then treated with distilled water which resulted in the cracking of the material into small granules with slight evolution of heat.

Ion-exchange capacity:

A 0.5 g of exchanger in Cl^- form was put into the glass column containing glass wool pack. It was washed with

distilled water to remove excess ions remained sticking on the particles. One molar solution of sodium nitrate was passed through the column the Cl^- so liberated was determined titrimetrically ( ).

Chemical stability:

A 0.2 gm of exchanger ZTP (222), Table-8 was equilibrated with 25 ml of the solution of interest at room temperature and kept for 24 hrs with occasional shaking. Zirconium ion released in the solution was determined titrimetrically using xylenol orange(4). Piperidine was determined spectrophotometrically using,1-chloro, 2-4 dinitro benzene (5) as a coloring reagent. Thioglycolic acid was determined spectrophotometrically (6).

Chemical composition:

For the determination of chemical composition of the samples, 0.1 gm of exchangers were dissolved in the minimum amount of hot concentrated sulfuric acid. Then the solution was diluted to 100 ml with distilled water. The zirconium was determined titrimetrically (4) while piperidine and thioglycolic acid was determined spectrophotometrically(5,6). The results are reported in Table-9.

Infrared spectrum:

Infra red spectrum of exchanger was performed using KBr technique.

Sorption Capacity and Distribution coefficient:

The distribution coeffecients for different metal ions were determined at different pH 0.2 g of exchanger was taken in 250 ml Erlenmeyer flask and to this a 25 ml of 2×10^{-3}M metal salt solution at different pH was added into different flask. The mixture was kept for 24 hrs at room temperature. The amount of metal species left in the solution was then determined by titrating against the standard solution of EDTA. The sorption capacities were determined as usual (7) while the Kd values were calculated according to the formula;

$$Kd = \frac{\text{mmoles of metal species/gm of exchanger}}{\text{mmoles of metal species/ml of the total volume of the resultant solution}}$$

The results are summarised in the tables 10 & 11.

Separation of metal ions:

Quantitative separations of metal ions were achieved on a 0.6 cm diameter (i.d.) glass column using 2.0 g exchanger. A metal ion mixture was poured on the top of the column. The flow rate of the effluent was maintained at 1 ml/min throughout the elution process (Table 12).

RESULTS AND DISCUSSION

Table-7 describes the preparation of different samples of zirconium piperidine thioglycolate exchanger. It is apparent from the table that ion exchange capacity has increased on adding thioglycolate component in the mixture. Its sorption capacity is increasing with the increase in thioglycolate content, while Sorption Capacity is zero for zirconium piperidine sample. Thus it is clear that thioglycolate part of exchanger is responsible for sorption of metals by the exchanger.

The sorption capacity of some transition metal ions due to thioglycolate interaction are, in accordance with the studies of formation constants of metal thioglycolate complexes, summarized in Table 10.

It is clear from the Table 8 that sample ZTP 222 is more stable in moderate concentration of NaOH, NH_3 HNO_3 but the samples get dissolved in INH_2SO_4.

The preparation of spherical beads of ZrO_2 has been described by adding phosphoric acid to zirconyl nitrate solution. The acid is sprayed into a column of mineral oil. Instead of using phosphoric acid one can also use NH_4OH (8). In order to get zirconium oxide particle we extended the idea of adding organic bases. The capacities

TABLE - 7

CONDITIONS OF SYNTHESIS AND SOME PROPERTIES OF ION EXCHANGE MATERIAL

Sample	Order of Mixing			Mixing Ratio	pH	Appearance of Beads	Ion Exchange capacity (Meq/g dry exchange)	sorption of Cu^{+2} mmol/g of exchanger
	I Component	II Component	III Component					
ZTP(222)	.2M Zirconium oxychloride	2M Thioglycolic acid	.2M Piperidine	2:1:2	1.63	White opaque	0.8775	0.25
ZPT 222	.2M Zirconium oxy chloride	.2M Piperidine	2M Thioglycolic acid	2:2:1	1.5	,,	0.7033	0.17
ZTP 212	.2M Zirconium oxy chloride	1M Thioglycolic acid	.2M Piperidine	2:1:2	2.0	,,	0.8840	0.09
ZTP 252	.2M Zirconium oxychloride	.5M Thioglycolic acid	.2M Piperidine	2:1:2	No Gel formation		-	-
ZT	.2M Zirconium oxychloride	2M Thioglycolic acid	-	2:1	,,		—	—
ZP	.2M Zirconium oxychloride	.2M Piperidine	-	1:1	2.6	White shiny	0.58	0.00

TABLE - 8

DETERMINATION OF CHEMICAL STABILITY OF DIFFERENT SAMPLES OF EXCHANGERS

Solution	Sample	Zirconium released mg/25	Thioglycolic Acid Mg/25 ml	Piperidine released mg/25 ml
1N Naoh	ZTP 222	0.0466	20.734	0.051
	ZTP 212	0.046	17.739	0.102
	ZPT 222	4.561	20.964	0.026
$1NNH_3$	ZTP 222	3.795	17.739	0.111
	ZTP 212	3.831	15.666	0.183
	ZPT 222	11.403	16.357	0.327
$2NHNO_3$	ZTP 222	0.00	0.00	0.00
	ZTP 212	0.00	0.00	0.00
	ZPT 222	0.00	0.00	0.00
$1NHNO_3$	ZTP 222	0.114	20.734	0.353
	ZTP 212	0.114	25.341	0.455
	ZPT 222	9.122	34.556	0.162
$1NH_2SO_4$	ZTP 222	←-------- dissolved completely -------→		
	ZTP 212	"		
	ZPT 222	"		

of hydrous zirconium oxide varies as a function of pH as well as the change of character from cation to anion exchanger (9). The protonated surface species, formed by the addition of piperidine, has acidic surface O-H group to which the piperidine react and form pip----H^+---pip. The piperidinium ionic species can be detected by the characteristic vib. modes. The normal N-H stretching modes are observed at about 1485-1500, 1540, 1620, 1640 cm^{-1}. Some times the detection of these protonated species is difficult due to a very short life time and hence a diffuse continuous absorption over the whole spectral range may be observed (10). It is clear from the I.R. spectra of zirconium piperidine exchanger in figure 9., from 1470 to 1700 cm^{-1}.

After the interaction the nitrogen atom gets positively charged and compensated by an equivalent amount of counter ion species and hence acting as an anion exchanger. N^+H species formation is supported by the infra red spectra (Fig 9 and 10) by the peak 2000 cm^{-1} and 2200 cm^{-1}. This interaction may be treated as a layer which is exactly equivalent to α-ZrP/α SnP layers. Intercalation of the guest molecule takes place between the two zirconium piperidine layers which can be visualized.

TABLE - 9

CHEMICAL COMPOSITION OF VARIOUS SAMPLES OF EXCHANGER

S.No.	SAMPLE	Zirconium mmoles	Thioglycolic Acid mmoles	Piperidine mmoles
1	ZTP 222	.550	.385	.019
2	ZTP 212	.470	.356	.005
3	ZPT 222	.480	.310	.018

TABLE 10

SORPTION CAPACITY OF DIFFERENT METALS ON ZTP 222 SAMPLE OF EXCHANGER

METAL ION	SORPTION CAPACITY mmole/g	METAL CHELATE TYPE	
		MRS (f1)	$M(RS_2)$ (f2)
Fe^{+++}	0.01	-	-
Fe^{+2}	-	-	1.7×10^{10}
Mn^{+2}	-	2.4×10^{4}	3.6×10^{7}
Co^{+2}	0.180	6.9×10^{5}	1.4×10^{12}
Ni^{+2}	0.015	9.5×10^{6}	3.4×10^{1}
Zn^{+2}	0.17	7.2×10^{7}	1.1×10^{15}
Cu^{+2}	0.183	-	-

TABLE- 11

Kd VALUES AT DIFFERENT pH IN ZTP 222 SAMPLE

S.No.	Metal	pH2	pH-4	pH-6	pH-8	pH-10
1	Cu^{+2}	292.00	∞	226.70	40.00	∞
2	Zn^{+2}	0.00	140.00	140.00	283.00	500.00
3	Cd^{+2}	3.20	6.66	6.66	6.66	4700.00
4	Ni^{+2}	7.90	151.43	96.00	76.00	66.00
5	Hg^{+2}	2300.00	0.00	200.	ppt	∞
6	Mn^{+2}	60.00	96.00	104.	81.48	122.72
7	Cr^{+3}	19.04	8.69	8.69	ppt	325.17
8	Fe^{+3}	0.00	76.00	100.00	340.00	*
9	Zr^{+4}	100.00	0.00	76.00	ppt	*
10	Th^{+4}	0.00	0.00	0.00	ppt	*
11	Co^{+2}	Brown	precipitate was formed			
12	Al^{+3}	∞	∞	∞	260.00	∞
13	UO_2^+	∞	∞	∞	∞	∞

....2

TABLE-11 continued

S.No.	Metal	pH-2	pH-4	pH-6	pH-8	pH-10
14	Tl^{+}	87.20	1660.00	∞	∞	∞
15	Bi^{+2}	200.00	28.00	162.00	ppt	*
16	Mg^{+2}	0.00	0.00	0.00	128.00	16.67
17	Pb^{+2}	264.24	300.80	125.80	ppt	∞
18	Ag^{+1}	<-- Precipitation occured ----------				

pH-2 0.2MKCl^{+}.2MHCl
pH-4 0.2MCH_3COONa+0.2M CH_3COOH (1:9)
pH-6 0.2MCH_3COONa+0.2MCH_3COOH (9:1)
pH-8 0.2M Citric Acid+.2M Na_2HPO_4
pH-10 NH_3+ NH_4Cl

* end point not clear
∞ v.v. high values

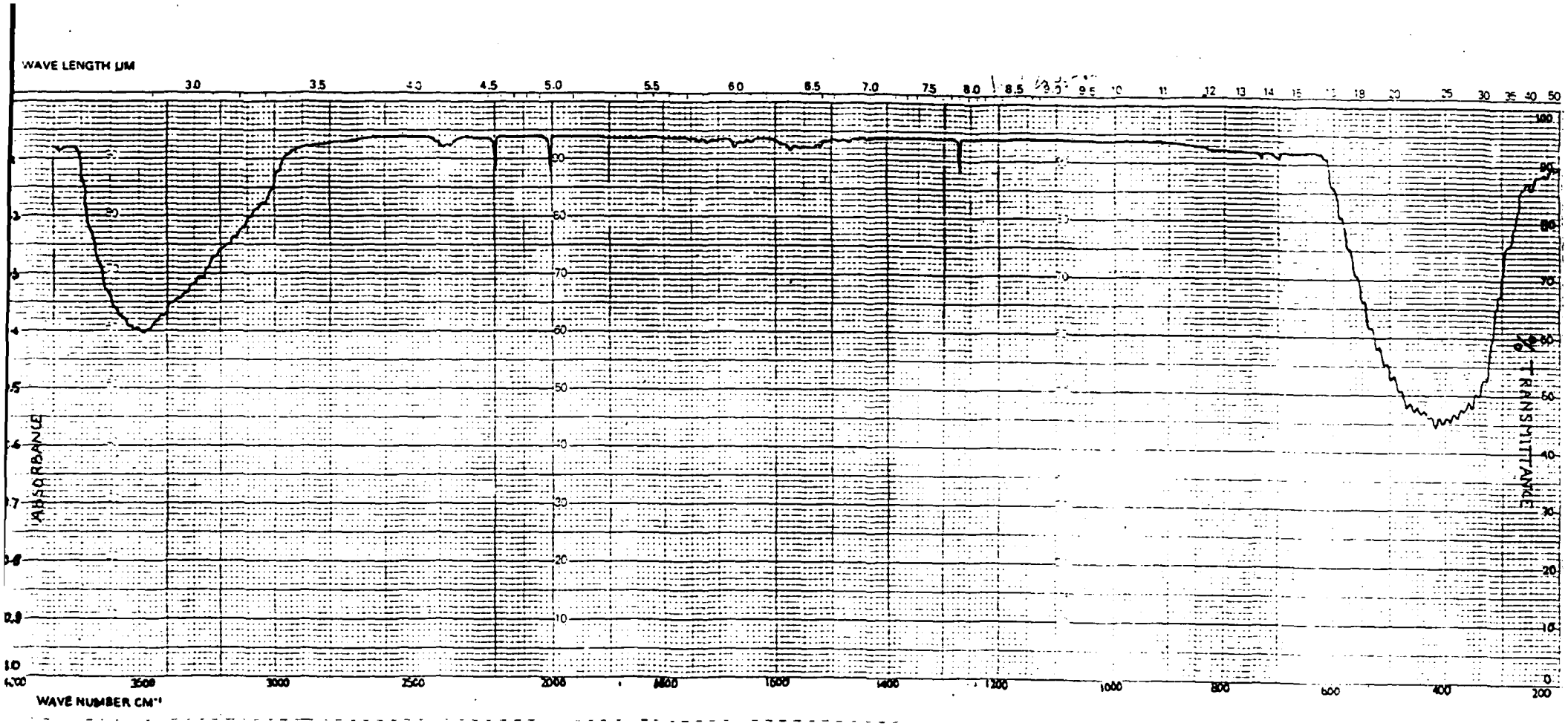


FIGURE 9 - INFRA RED SPECTRUM OF ZIRCONIUM PIPERDINE EXCHANGER.

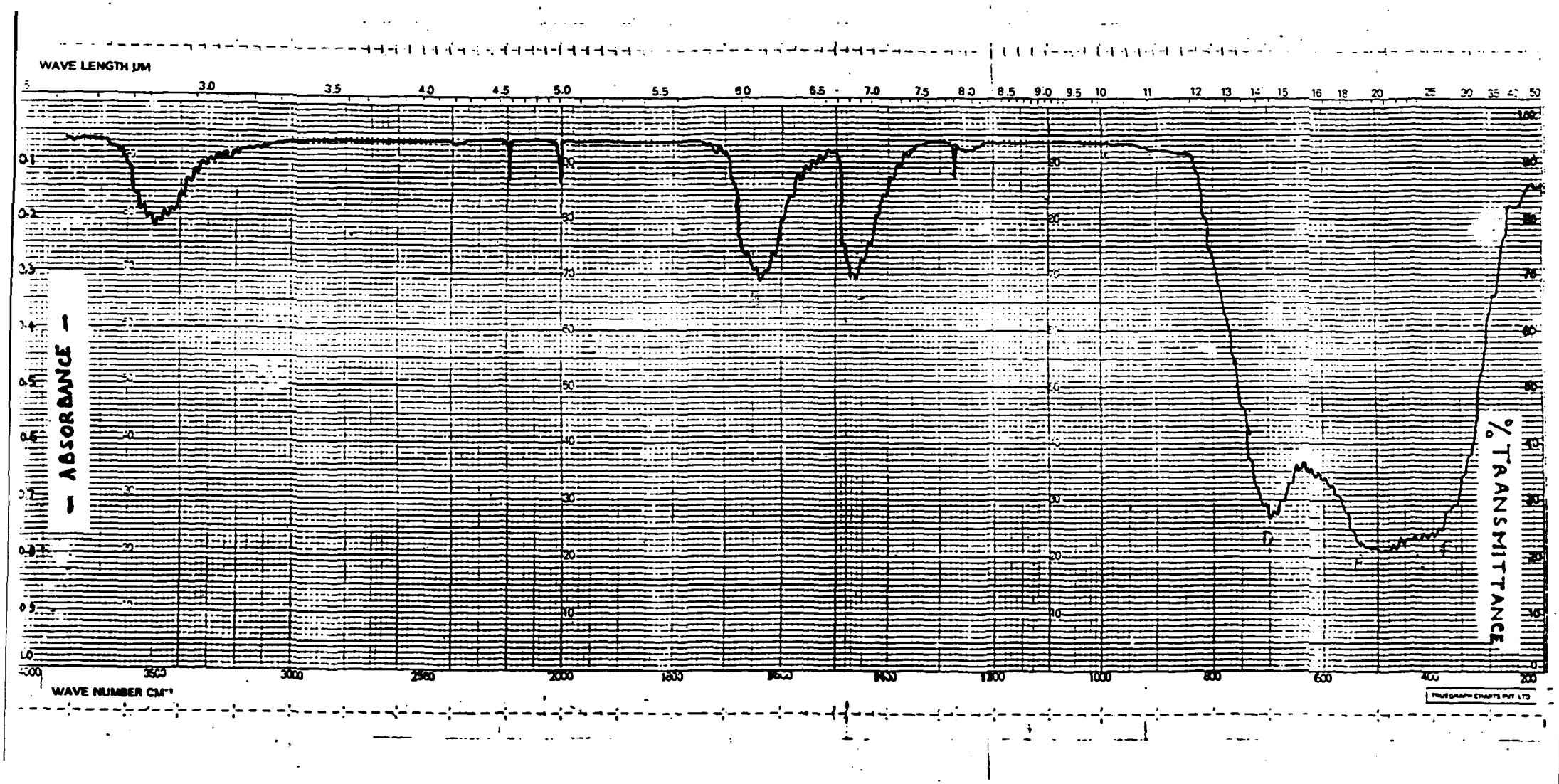
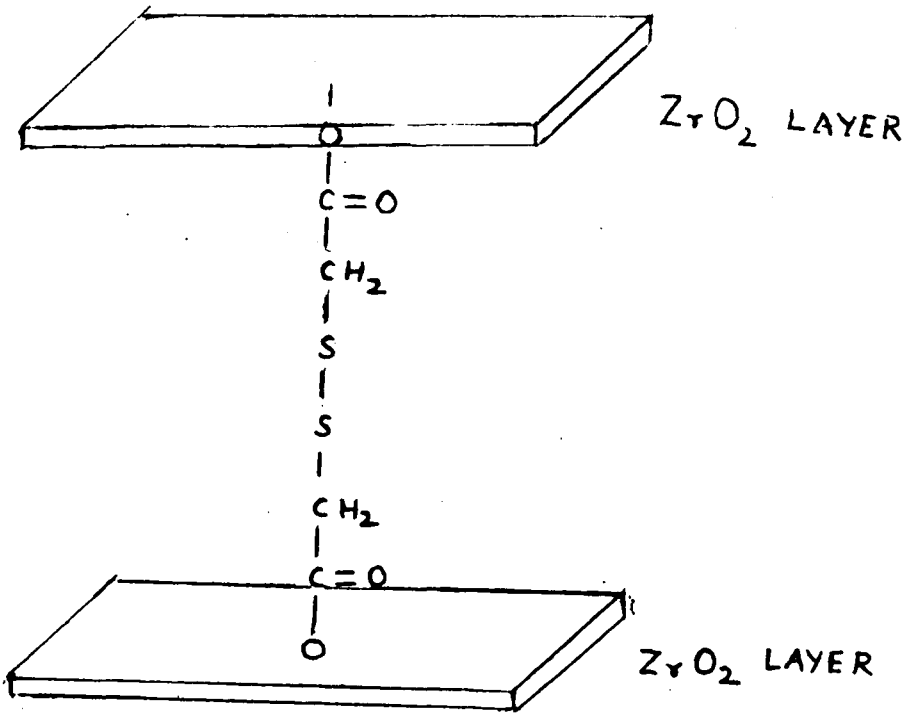


FIGURE 10 - INFRA RED SPECTRUM OF ZIRCONIUM PIPERIDINE THIOGLYCOLATE EXCHANGER.



IR Discussion

(1) 400-450 cm^{-1} bands are assigned to ZrO_2.

(2) S-S stretching vibrations fall between 400-500 cm^{-1}.

(3) The stretching vibration assigned to C-S linkage occure in the region of 700 cm^{-1}.

(4) A sharp band of C-N stretching in aromatic amine is assigned to 1350 to 1280. Piperidine cyclic ring is analog to aromatic ring and therefore C-N stretching must fall in this range.

(5) In the liquid or solid state carboxylic acids exist as dimers due to H-bonding. The C=O stretching frequency observed at 1650 may be attributed due to internal hydrogen bonding. C=O stretching of COOH group appears at 1460. There appears no bending (1320-1210) due to intercalation resulting the formation of Zr-O bonding.

(6) Two strong peaks 2000 & 2200 may be attributed to NH^+.

So the study of transition metals is the formation of stable complexes of thioglycolic acids. Earlier studies reveal the formation of two types of complexes MRS and $M(RS)_2^=$ . . (11).

This exchanger is therefore has a dual character. Anion species can be exchanged with piperidine group and cation exchange with specially transition metals with thioglycolic acid.

The distribution coeffecient(Kd) for a number of metals ions were determined at different pH values. The stability of metal ligand complex depends upon the pH of the equilibrating solution, results in the variation in the extent of uptake of a metal ion. The Kd values for UO_2^{2+} and Al^{3+} are very high in all the solvents except pH 8.0 where it is somewhat lower for Al^{3+}.

On the basis of large differences in sorption of the metal ions at different pH, a number of separations have been achieved. Results are summarized in Table 12 and elution profiles are shown in figure 11.

TABLE -12

SOME BINARY METAL IONS SEPARATION ACHIEVED ON ZTP 222 SAMPLE OF EXCHANGER

S.No.	Separation Achieved	Amount Loaded mg	Amount Found mg	Percent Recovery	Vol of Effluent	Composition of Eluent
1	Zn^{+2}	0.784	0.680	86.67 %	40 ml	pH-2 Buffer
	Hg^{+2}	1.926	2.036	105.7 %	50 ml	.2M HNO_3
2	Ni^{+2}	0.518	0.524	101.13 %	50 ml	pH-2 Buffer
	Hg^{+2}	1.926	1.996	103.6 %	60 ml	.2M HNO_3
3	Fe^{+3}	0.492	0.480	97.72 %	60 ml	pH-2 Buffer
	Hg^{+2}	1.926	2.056	106.77 %	50 ml	.2M HNO_3
4	Al^{+3}	0.194	0.196	102.77 %	60 ml	pH-2 Buffer
	Hg^{+2}	1.926	2.046	106.25 %	50 ml	.2M HNO_3

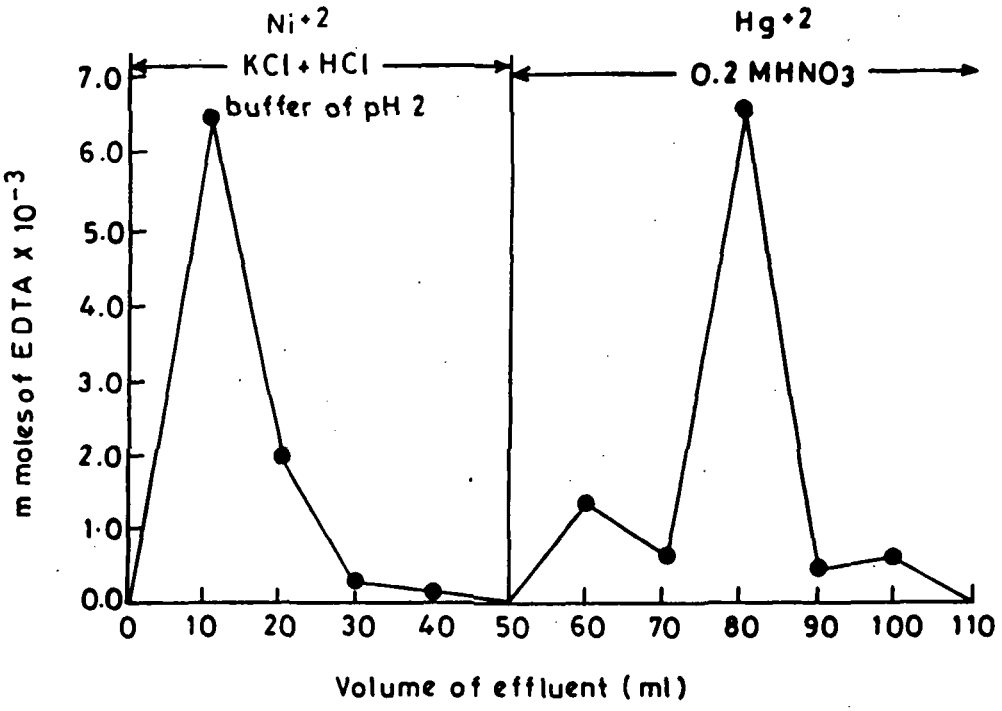


Fig.11 (c) - Separation of Hg^{2+} from Ni^{2+}

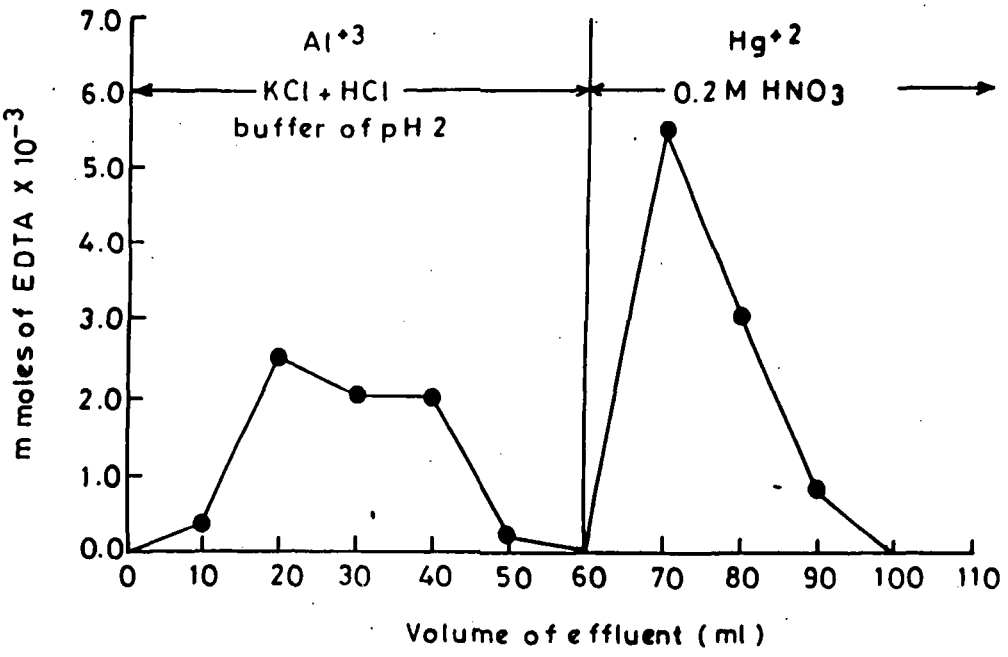


Fig.11 (d) - Separation of Al^{3+} from Hg^{2+}

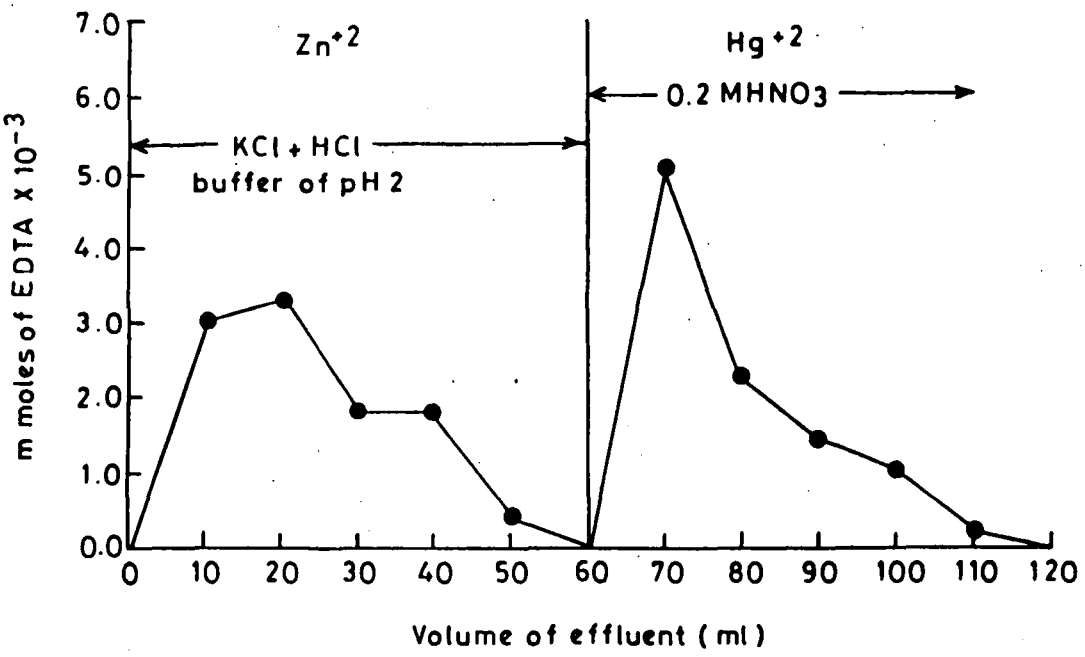


Fig.11(a) - Separation of Hg^{2+} from Zn^{2+}

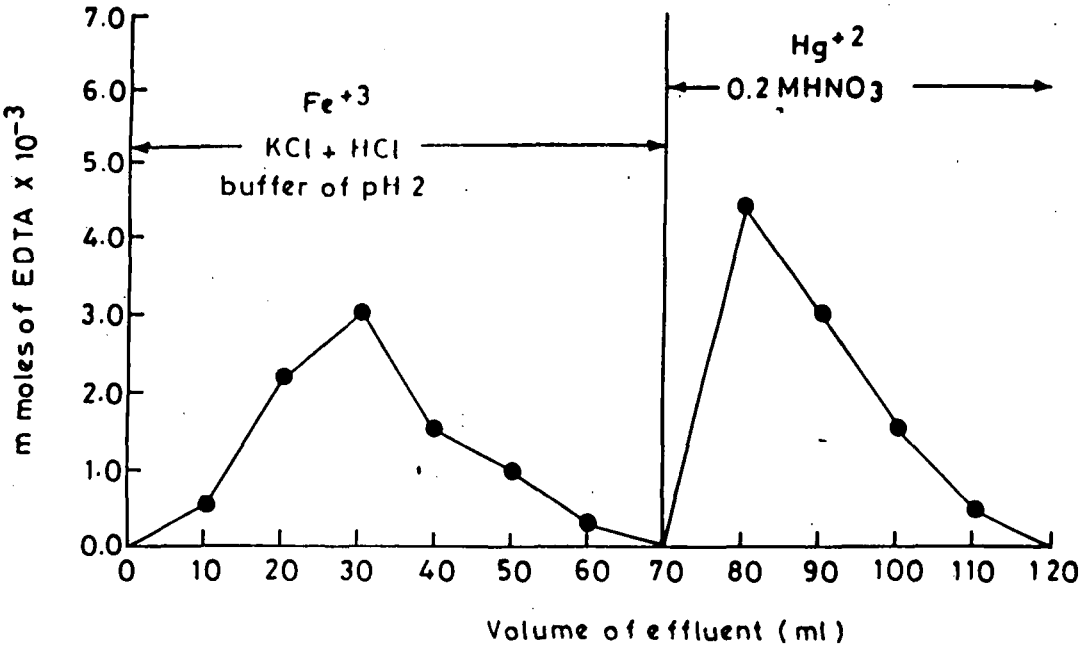


Fig.11(b) - Separation of Hg^{2+} from Fe^{3+}

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